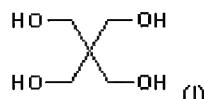


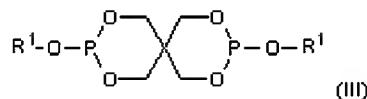
Claims

[c1] 1. An improved method for synthesizing pentaerythritol diphosphites comprising the steps of:

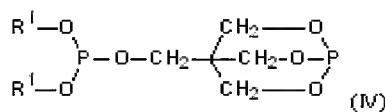
(a) transesterifying pentaerythritol of formula (I)



with a monophosphite to form a first reaction mixture which comprises an intermediate pentaerythritol diphosphite having a spiro isomer as shown in the following formula (III),



a caged isomer shown in the following formula (IV),



unreacted monophosphite and side reaction products wherein R^1 is selected from the group consisting of wherein R^1 is selected from the group consisting straight-chain or branched C_{1-20} alkyl groups, C_{5-7} cycloaliphatic groups and C_{6-11} substituted derivatives thereof, straight-chain or branched C_{2-30}

alkenyl groups, C_{6-18} aryl groups, C_{7-40} alkylaryl groups and C_{7-40} arylalkyl groups and blends thereof;

(b) removing reaction products other than said intermediate pentaerythritol diphosphite from said first reaction mixture; and

(c) transesterifying said intermediate pentaerythritol diphosphite with an alcohol selected from the group consisting of C_{8-22} alkanols, C_{8-22} alkenols, phenols, C_{7-40} alkylaryl alcohols and C_{7-40} arylalkyl alcohols to form a second reaction mixture which comprises a final pentaerythritol diphosphite of formula (VI)



where R^2 is selected from the group consisting of C_{8-22} alkyls, C_{8-22} alkenyls, phenyl, C_{7-40} alkylaryls and C_{7-40} arylalkyls.

- [c2] 2. The method of claim 1 which further comprises the step of separating said intermediate pentaerythritol diphosphite from said first reaction mixture to produce a purified intermediate pentaerythritol diphosphite.
- [c3] 3. The method of claim 2 wherein said monophosphite is selected from the group consisting of trimethyl phosphite, triethyl phosphite and triphenyl phosphite.

- [c4] 4. The method of claim 3 wherein said monophosphite is triphenyl phosphite.
- [c5] 5. The method of claim 4 wherein said intermediate pentaerythritol diphosphite is diphenyl pentaerythritol diphosphite.
- [c6] 6. The method of claim 1 wherein a ratio of said monophosphite to said pentaerythritol is about 2 moles of monophosphite per mole of pentaerythritol.
- [c7] 7. The method of claim 1 which further comprises an alkaline catalyst.
- [c8] 8. The method of claim 1, wherein said amount of said alkaline catalyst ranges from about 0.01 weight percent to about 5 weight percent, based on the intermediate pentaerythritol diphosphite.
- [c9] 9. The method of claim 1 wherein said alcohol is 2,4-dicumyl phenol.
- [c10] 10. The method of claim 1, wherein said first transesterification reaction pressure is in a range from about 0.01 mm Hg to about 100 mm Hg.
- [c11] 11. The method of claim 10 wherein said first transesterification reaction temperature is in a range from about

70°C to about 105°C.

- [c12] 12. The method of claim 11 wherein said first reaction mixture further comprises a solvent.
- [c13] 13. The method of claim 12, wherein said solvent is selected from the group consisting of C₆ – C₂₀ aromatic hydrocarbons and C₆ – C₂₀ aliphatic hydrocarbons and blends thereof.
- [c14] 14. The method of claim 13, wherein said solvent is added in an amount ranging from about 10 weight percent to about 200 weight percent of said intermediate pentaerythritol diphosphite.
- [c15] 15. The method of claim 11 wherein said intermediate pentaerythritol diphosphite comprises a spiro isomer content of greater than 90 percent.
- [c16] 16. The method of claim 15 wherein said intermediate pentaerythritol diphosphite has a yield of greater than 95 percent, based on the monophosphite.
- [c17] 17. The method of claim 2 wherein said separating step comprises distillation of said reaction mixture sufficient to purify said intermediate pentaerythritol diphosphite to a purity of at least 99 percent.
- [c18] 18. The method of claim 17 wherein the purity of said

intermediate pentaerythritol diphosphite is at least 99.9 percent.

- [c19] 19. The method of claim 2 further comprising the step of separating said second pentaerythritol diphosphite from said second reaction mixture.
- [c20] 20. The method of claim 19 wherein said step of separating said second pentaerythritol diphosphite from said second reaction mixture comprises a step of distillation.
- [c21] 21. The method of claim 19 wherein said alcohol is selected from the group consisting of 2,4-di-t-butylphenol and 2,4-dicumylphenol.
- [c22] 22. The method of claim 21 wherein said alcohol is 2,4-dicumylphenol.
- [c23] 23. The method of claim 19 wherein said final pentaerythritol diphosphite is selected from the group consisting of bis(2,4-dicumylphenyl) pentaerythritol diphosphite and bis (2,4-di-t-butylphenyl) pentaerythritol diphosphite.
- [c24] 24. The method of claim 19 wherein said second temperature is in a range of about 130°C to about 170°C.
- [c25] 25. The method of claim 24 wherein said second pressure is in a range of about 0.01 mm Hg to about 100

mm Hg.

- [c26] 26. The method of claim 19, wherein the amount of said alcohol ranges from about 2 moles to about 8 moles per mole of said intermediate pentaerythritol diphosphite.
- [c27] 27. The method of claim 19, which further comprises a second alkaline catalyst.
- [c28] 28. The method of claim 27, wherein the amount of said second alkaline catalyst is in a range of about 0.01 weight percent to about 5 weight percent, based on the final pentaerythritol diphosphite.
- [c29] 29. The method of claim 19, wherein said final pentaerythritol diphosphite comprises a spiro isomer content of greater than 90 mole percent.
- [c30] 30. An improved method for synthesizing pentaerythritol diphosphites comprising the steps of:
 - (a) transesterifying pentaerythritol with a monophosphite to form a first reaction mixture which comprises an intermediate pentaerythritol diphosphite having a spiro and a caged isomer and unreacted monophosphite and side reaction products at a temperature below 125°C;
 - (b) removing reaction products other than said intermediate pentaerythritol diphosphite from said first

reaction mixture; and

(c) transesterifying said intermediate pentaerythritol diphosphite with an excess of an alcohol to form a second reaction mixture which comprises a final pentaerythritol diphosphite at a temperature below 175°C, said final pentaerythritol diphosphite having a spiro content in excess of 90 mole percent without purification by recrystallization.

- [c31] 31. The method of claim 30 which further comprises the step of separating said intermediate pentaerythritol diphosphite from said first reaction mixture to produce a purified intermediate pentaerythritol diphosphite.
- [c32] 32. The method of claim 31 wherein said monophosphite is selected from the group consisting of trimethyl phosphite, triethyl phosphite and triphenyl phosphite.
- [c33] 33. The method of claim 32 wherein said monophosphite is triphenyl phosphite.
- [c34] 34. The method of claim 33 wherein said intermediate pentaerythritol diphosphite is diphenyl pentaerythritol diphosphite.
- [c35] 35. The method of claim 30 wherein a ratio of said monophosphite to said pentaerythritol is about 2 moles of monophosphite per mole of pentaerythritol.

- [c36] 36. The method of claim 30 which further comprises an alkaline catalyst.
- [c37] 37. The method of claim 30, wherein said amount of said alkaline catalyst ranges from about 0.01 weight percent to about 5 weight percent, based on the intermediate pentaerythritol diphosphite.
- [c38] 38. The method of claim 30 wherein said alcohol is 2,4-dicumyl phenol.
- [c39] 39. The method of claim 30, wherein said first transesterification reaction pressure is in a range from about 0.01 mm Hg to about 100 mm Hg.
- [c40] 40. The method of claim 39 wherein said first transesterification reaction temperature is in a range from about 70°C to about 105°C.
- [c41] 41. The method of claim 40 wherein said first reaction mixture further comprises a solvent.
- [c42] 42. The method of claim 41, wherein said solvent is selected from the group consisting of C₆ – C₂₀ aromatic hydrocarbons and C₆ – C₂₀ aliphatic hydrocarbons and blends thereof.
- [c43] 43. The method of claim 42, wherein said solvent is

added in an amount ranging from about 10 weight percent to about 200 weight percent of said intermediate pentaerythritol diphosphite.

- [c44] 44. The method of claim 30 wherein said intermediate pentaerythritol diphosphite comprises a spiro isomer content of greater than 90 percent.
- [c45] 45. The method of claim 44 wherein said intermediate pentaerythritol diphosphite has a yield of greater than 95 percent, based on the monophosphite.
- [c46] 46. The method of claim 31 wherein said separating step comprises distillation of said reaction mixture sufficient to purify said intermediate pentaerythritol diphosphite to a purity of at least 99 percent.
- [c47] 47. The method of claim 46 wherein the purity of said intermediate pentaerythritol diphosphite is at least 99.9 percent.
- [c48] 48. The method of claim 31 further comprising the step of separating said second pentaerythritol diphosphite from said second reaction mixture.
- [c49] 49. The method of claim 48 wherein said step of separating said second pentaerythritol diphosphite from said second reaction mixture comprises a step of distillation.

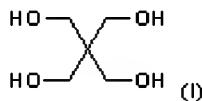
- [c50] 50. The method of claim 48 wherein said alcohol is selected from the group consisting of 2,4-di-t-butylphenol and 2,4-dicumylphenol.
- [c51] 51. The method of claim 50 wherein said alcohol is 2,4-dicumylphenol.
- [c52] 52. The method of claim 48 wherein said final pentaerythritol diphosphite is selected from the group consisting of bis(2,4-dicumylphenyl) pentaerythritol diphosphite and bis (2,4-di-t-butylphenyl) pentaerythritol diphosphite.
- [c53] 53. The method of claim 48 wherein said second temperature is in a range of about 130°C to about 170°C.
- [c54] 54. The method of claim 53 wherein said second pressure is in a range of about 0.01 mm Hg to about 100 mm Hg.
- [c55] 55. The method of claim 48, wherein the amount of said alcohol ranges from about 2 moles to about 8 moles per mole of said intermediate pentaerythritol diphosphite.
- [c56] 56. The method of claim 48, which further comprises a second alkaline catalyst.
- [c57] 57. The method of claim 56, wherein the amount of said

second alkaline catalyst is in a range of about 0.01 weight percent to about 5 weight percent, based on the final pentaerythritol diphosphite.

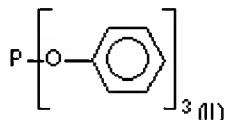
[c58] 58. The method of claim 48, wherein said final pentaerythritol diphosphite comprises a spiro isomer content of greater than 90 mole percent.

[c59] 59. An improved method for synthesizing bis(2,4-dicumylphenyl) pentaerythritol diphosphite comprising the steps of:

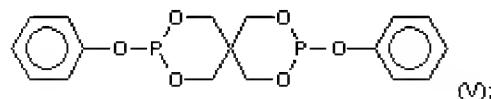
(a) transesterifying pentaerythritol of formula (I)



with triphenyl phosphite of formula (II)



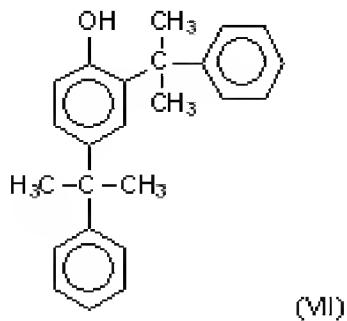
to form an intermediate reaction mixture comprising diphenyl pentaerythritol diphosphite of formula (V)



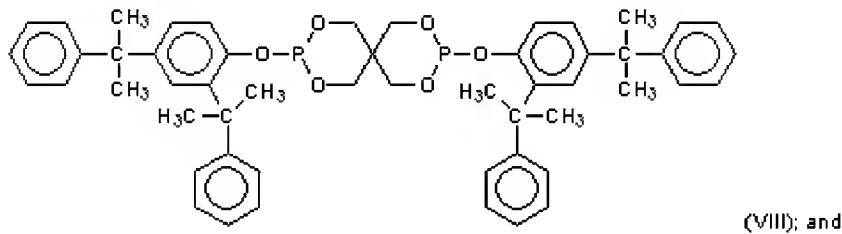
(b) removing phenol and reaction products other than diphenylpentaerythritol diphosphite from said intermediate reaction mixture;

(c) transesterifying said intermediate pentaerythritol

diphosphite with 2,4-dicumyl phenol of formula (VII)



to form a second reaction mixture which comprises a final pentaerythritol diphosphite bis(2,4-dicumylphenyl) pentaerythritol diphosphite of formula (VIII)



(d) removing phenol from said second reaction mixture.

- [c60] 60. The method of claim 59 wherein a ratio of said triphenyl phosphite to said pentaerythritol is about 2 moles of triphenyl phosphite per mole of pentaerythritol.
- [c61] 61. The method of claim 59 which further comprises an alkaline catalyst for said first transesterification reaction.
- [c62] 62. The method of claim 61, wherein said amount of said alkaline catalyst ranges from about 0.01 weight percent to about 5 weight percent, based on the intermediate

diphenyl pentaerythritol diphosphite.

- [c63] 63. The method of claim 62, wherein said first transesterification reaction pressure is in a range from about 0.01 mm Hg to about 100 mm Hg.
- [c64] 64. The method of claim 63 wherein said first transesterification reaction temperature is in a range from about 70°C to about 105°C.
- [c65] 65. The method of claim 64 wherein said first reaction mixture further comprises a solvent.
- [c66] 66. The method of claim 65, wherein said solvent is selected from the group consisting of C₆ – C₂₀ aromatic hydrocarbons and C₆ – C₂₀ aliphatic hydrocarbons and blends thereof.
- [c67] 67. The method of claim 66, wherein said solvent is added in an amount ranging from about 10 weight percent to about 200 weight percent of said intermediate diphenyl pentaerythritol diphosphite.
- [c68] 68. The method of claim 67 wherein said intermediate diphenyl pentaerythritol diphosphite comprises a spiro isomer content of greater than 90 percent.
- [c69] 69. The method of claim 68 wherein said intermediate diphenyl pentaerythritol diphosphite has a yield of

greater than 95 percent, based on the triphenyl phosphite.

- [c70] 70. The method of claim 59 wherein said step of removing phenol from said first reaction mixture comprises distillation.
- [c71] 71. The method of claim 70 wherein said step of removing phenol from said reaction mixture purifies said intermediate diphenyl pentaerythritol diphosphite to a purity of at least 99 percent.
- [c72] 72. The method of claim 71 wherein the purity of said intermediate diphenyl pentaerythritol diphosphite is at least 99.9 percent.
- [c73] 73. The method of claim 70 wherein said step of removing phenol from said second reaction mixture comprises distillation.
- [c74] 74. The method of claim 73 wherein said second temperature is in a range of about 130°C to about 170°C.
- [c75] 75. The method of claim 74 wherein said second pressure is in a range of about 0.01 mm Hg to about 100 mm Hg.
- [c76] 76. The method of claim 75, wherein the amount of said 2,4-dicumyl phenol ranges from about 2 moles to about

8 moles per mole of said intermediate diphenyl pentaerythritol diphosphite.

- [c77] 77. The method of claim 76, which further comprises a second alkaline catalyst for said second transesterification step.
- [c78] 78. The method of claim 77, wherein the amount of said second alkaline catalyst is in a range of about 0.01 weight percent to about 5 weight percent, based on the bis(2,4-dicumylphenyl) pentaerythritol diphosphite.
- [c79] 79. The method of claim 78, wherein said final bis(2,4-dicumylphenyl) pentaerythritol diphosphite comprises a spiro isomer content of greater than 90 mole percent.
- [c80] 80. The method of claim 1, which further comprises a step of recycling at least a portion of said reaction products other than said intermediate pentaerythritol diphosphite from said first reaction mixture.
- [c81] 81. The method of claim 80, wherein said step of recycling comprises a step of recycling phenol.
- [c82] 82. The method of claim 80, which further comprises a step of recycling at least a portion of said reaction products other than said final pentaerythritol diphosphite

from said second reaction mixture.

- [c83] 83. The method of claim 82, wherein said step of recycling comprises a step of recycling 2,4-dicumyl phenol.
- [c84] 84. The method of claim 30, which further comprises a step of recycling at least a portion of said unreacted monophosphite or said side reaction products.
- [c85] 85. The method of claim 84, wherein said step of recycling comprises a step of recycling phenol.
- [c86] 86. The method of claim 84, which further comprises a step of recycling at least a portion of said alcohol.
- [c87] 87. The method of claim 86, wherein said alcohol is 2,4-dicumyl phenol.
- [c88] 88. The method of claim 59, which further comprises a step of recycling at least a portion of said first reaction mixture selected from the group consisting of triphenyl phosphite, phenol and reaction products.
- [c89] 89. The method of claim 88 which further comprises a step of recycling at least a portion of said second reaction mixture selected from the group consisting of 2,4-dicumyl phenol and phenol.